

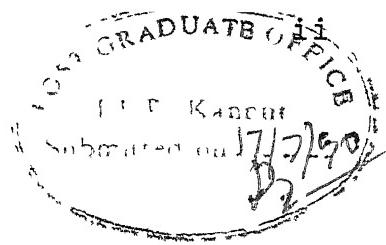
PHOSPHATE ADSORPTION - DESORPTION EXPERIMENTS WITH RIVER CLAY MINERALS UNDER UPPER ESTUARY CONDITION

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

by
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to the
DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
JULY, 1990

CERTIFICATE



It is certified that the work contained in the thesis entitled "Phosphate Adsorption-Desorption Experiments with River Clay Minerals under Upper Estuary condition" has been carried out by Sri Sansaya Kumar Bisoi under my supervision and that this work has not been submitted elsewhere for a degree.

July, 1990

A handwritten signature in black ink, appearing to read "B.C. Raymahashay".

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ABSTRACT

Experiments were designed to study phosphate uptake at room temperature by typical river suspended material like kaolinite clay (with illite, quartz), lateritic soil (kaolinite, gibbsite, iron oxide with quartz) and black cotton soil (montmorillonite with feldspar). Hundred percent adsorption was observed for lateritic soil from 2 mg/l phosphate solution. Phosphate uptake was progressively lower for black cotton soil and kaolinite. For all these three materials, phosphate adsorption was less when 2 mg/l phosphate was dissolved in NaCl-NaHCO₃ solutions of ionic strength 0.3 and pH around 8. This implied that phosphate-sediment interaction would vary with the clay mineralogy of the suspended matter which in turn will be controlled by the geology of the drainage basin. At the same time, phosphate uptake by river sediments would decrease from fresh water to sea-water mixing zone in the upper estuary.

Complementary experiments with acidified phosphate solution showed an increase in adsorption. On the other hand, uptake was less for a higher initial concentration of 5 mg/l phosphate solution.

A series of desorption experiments confirmed the above conclusions. Desorption into distilled water was slightly higher for black cotton soil, compared with lateritic

soil. Desorption from black cotton soil was even higher into salt solution. This supported data from actual estuaries which indicate that phosphate adsorbed by river sediments in the fresh water zone may be released in the saline zone. Maximum desorption (52%) was obtained from black cotton soil in 5 mg/l phosphate solution.

CHAPTER 1

INTRODUCTION AND OBJECTIVE

Among minor constituents of river water, phosphate has great environmental significance. Along with carbon and nitrogen compounds, it acts as a nutrient in photosynthesis reaction. The resulting excess growth of algae at river mouth leads to eutrophication problems. Therefore, geo-chemists and environmental scientists are keen to monitor the phosphate budget during mixing of river and sea water. At the same time, considerable data have been collected (Moore and Silver, 1975) which indicate that lake sediments act as a sink for dissolved phosphate. This is mainly through the process of ion exchange and adsorption by clay minerals. In a manner similar to trace elements and toxic metals, the fixation of phosphate on clay minerals is also believed to be sensitive to salinity. Berner and Berner (1987) summarise that inorganic removal of Si, P, Fe etc. in estuaries is complete around 15 ppt salinity. Moreover, clay minerals are in suspension only in the upper estuary where salinity values are below the range of 1 to 3 ppt. At greater salinity towards the open sea, the clay particles are cohesive and there is no important change beyond the initial mixing of fresh and saline water. Therefore, at the region where the river meets the sea, there is a possibility that phosphate adsorption may be reduced or reversed. In fact, most of the field data on phosphate in

estuary have been collected in the low-salinity zone.

Previous work (for example Mehta, 1982) has also indicated that the uptake of an anion like PO_4^{3-} will be more efficient in lateritic soils which contain positively charged iron oxide/hydroxide colloids in addition to clay minerals.

It would be obvious from the above discussion that transport of phosphate by clay minerals suspended in river water will depend upon several factors including (1) type of clay (2) phosphate level (3) presence of other components like iron oxide, organic matter etc. in the sediments and (4) change in salinity in the estuarine mixing zone. Keeping these factors in mind, it was decided to carry out an experimental investigation of the interaction between dissolved phosphate and typical river clay minerals.

Objective and Experimental Frame Work

The main approach of this experimental study can be summarised as follows:

- (1) To design batch experiments to monitor initial and final phosphate concentration in solutions kept in contact with selected clay minerals and soils. The type of clay minerals and other parameters like phosphate level, clay concentration,

equilibrium time etc. were selected on the basis of literature review.

- (2) To extend previous work by monitoring desorption of phosphate from the clay minerals and soils into distilled water and NaCl solution.
- (3) To introduce salinity, typical of the upper estuary zone as a component in the experimental runs and monitor phosphate adsorption and desorption as before.
- (4) To compare the behaviour of different clay minerals and soils and draw conclusions about the application of these data to actual river mouth condition.

CHAPTER 2

LITERATURE REVIEW

(i) Importance of Dissolved Phosphate

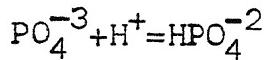
Study of dissolved phosphate is important for the following two reasons: (1) phosphate is introduced into rivers and other water bodies as a pollutant and is one of the principal causes for eutrophication (Moore and Silver, 1975; Sawyer and McCarty, 1978; Berner and Berner, 1987) (2) in agricultural practice, phosphate is introduced into the soil through fertilizers where efficiency of fertilizer application depends upon phosphate fixation by soil minerals (Sawyer and McCarty, 1978). Agricultural wastes, therefore, commonly contain dissolved phosphate. In their review of nutrient transport by sediments, Moore and Silver (1975) concluded that the minimum phosphate content in water below which eutrophication does not appear to be a problem is 0.01 mg/l. In contrast, the range of phosphate content in river and lake sediments at the minimum threshold of eutrophication is 14-400 mg/Kg. These authors, therefore, suggest an equilibrium partition ratio of the order of 1:10,000 between water and sediment. This points to the role of sediments as a sink for phosphate. According to Berner and Berner (1987), the major source of phosphate in the natural cycle is weathering of rocks. Human interference has come through

deforestation, use of fertilizers and detergents, production of industrial wastes and sewage. Pollution control requires an efficient method for the removal of phosphate from natural and waste water. This is achieved by treating the water with some material which can adsorb phosphate and this adsorbent should be cheap and easily available. Clay minerals satisfy these two conditions.

(ii) Dissolved Phosphate Species

Phosphorous is transported by river water in two principal forms, (1) dissolved (2) adsorbed. Out of a total of 2×10^{12} grams per year of dissolved phosphate transported in river run off, about half is present as inorganic phosphate, which is mostly orthophosphate ions (H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-}). The rest is believed to be dissolved organic phosphorous (Berner and Berner, 1987).

The distribution of the orthophosphate anions are pH dependent as shown by the following equilibrium constant values (Krauskopf, 1979).

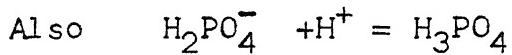
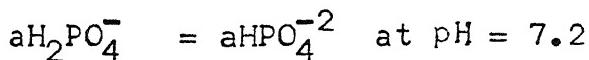


$$K_1 = \frac{aHPO_4^{2-}}{aPO_4^{3-} \cdot aH^+} = 10^{12.4}$$

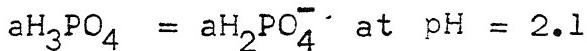
$$\text{Hence, } aHPO_4^{2-} = aPO_4^{3-} \text{ at pH } = 12.4$$

$$\text{Similarly, } HPO_4^{2-} + H^+ = H_2PO_4^-$$

$$K_2 = \frac{aH_2PO_4^-}{aHPO_4^{2-} \cdot aH^+} = 10^{7.2}$$



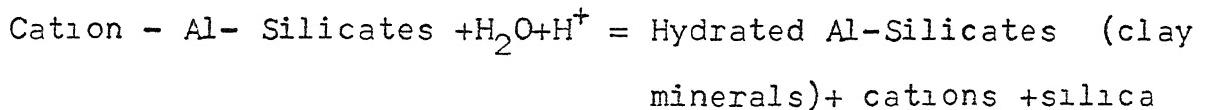
$$K_3 = \frac{aH_3PO_4}{aH_2PO_4^- \cdot aH^+} = 10^{2.1}$$



As mentioned earlier, the anionic orthophosphate species are adsorbed on river sediment because of positively charge sites on clays and iron oxide colloids and possibly on organic matter. Some details about the origin of clay minerals and the surface charge on clay particles are given below.

(iii) Origin of Clay Minerals

The major process by which the clay minerals are generated in the geochemical cycle is weathering of rocks. Most rock forming minerals are cation-Al-Silicates. Under the influence of moderately acidic natural water (for example, rain water), weathering reactions take place according to the following scheme.



It follows, therefore, that the type of clay mineral formed during weathering will depend upon the mineralogy

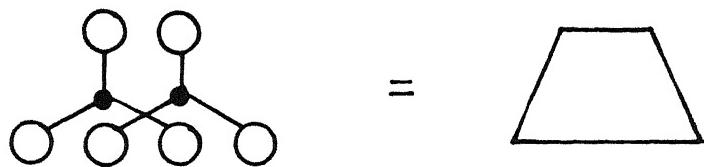
of the source rock and other physical parameters like temperature, rainfall, permeability, rate of removal of cations etc. Pettijohn (1984) has summarised the environment of formation of kaolinite type clay as granitic rocks, high rainfall, presence of joints and fractures, humid climate and acidic environment. In contrast, the montmorillonite type of clay minerals are developed from Fe-Mg rich (mafic) basaltic rocks, when cations accumulate due to poor drainage and the environment is relatively alkaline. The third important group of clay mineral is illite which is dominant in shales and marine sedimentary rocks. It has been suggested that the primary requirement for the formation of illite is abundant K^+ ions which is supplied by sea water (Krauskopf, 1979). There are field and experimental evidence showing conversion of montmorillonite to illite by K^+ fixation in the deltaic environment.

As a result of the above mentioned rock-water reactions, clay minerals are found in two distinct field situations (1) in suspended sediments and (2) in soils. In both, they are likely to be exposed to natural and waste water containing major and trace elements. (Wayman, 1967). Particularly the clay minerals present in suspended form in river water have large surface area per unit weight. Therefore, they operate as adsorbents and transport many environmentally significant elements present in the river water. At the same time, ion exchange and adsorption properties of clay minerals have been exploited to utilise

the clay minerals as decontamination devices (Raymahashay, 1987). In order to evaluate these reactions at the clay-water interface, we have to review the important features of clay minerals namely (iv) structure of clay minerals (v) size and shape (vi) exchange properties (vii) colloidal behaviour of clay.

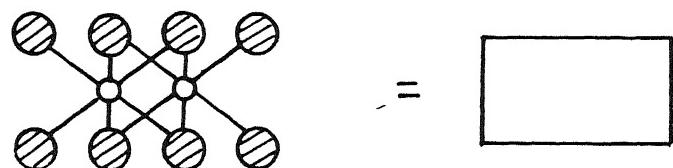
(iv) Structure of Clay Minerals

Two basic structural units are involved in the atomic lattice of clay minerals (1) Tetrahedral layer (T) which is built by sharing of three corners of SiO_4 tetrahedra with each other in the basal plane (Fig. 2.1a). The structural formula for this layer is Si_2O_5 with net -2 charge. (2) Octahedral layer (O) which is made of linked ($\text{Al}-\text{OH}$) octahedra (Fig. 2.1b) with structural formula $\text{Al}_2(\text{OH})_6$. Two dimensional extension of both 'T' and 'O' layers produce sheet structure of the clay minerals. This is the reason why the clay minerals have flaky shape. On the other hand, various structural types are produced by different linking of the 'T' and 'O' layers. For example, kaolinite is a typical two layer clay (Fig. 2.2a). Here one 'T' layer is linked with one modified 'O' layer. In the 'O' layer, two out of the six OH corners are common with oxygen. Therefore, the structural formula of kaolinite is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ with basal spacing of 7.2 Å. On the other hand both montmorillonite and illite are 3-layer minerals with one 'O' layer sandwiched between two 'T' layers. Four out of six 'OH' corners



● Silicon ○ Oxygen

a. Tetrahedral sheet



○ Aluminum ⓧ Hydroxyl

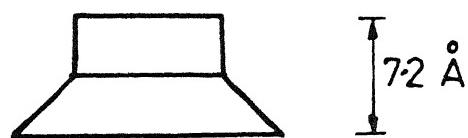
b. Octahedral sheet

Fig. 2.1 Schematic representation of tetrahedral and octahedral sheets. After Lambe and Whitman, 1967.

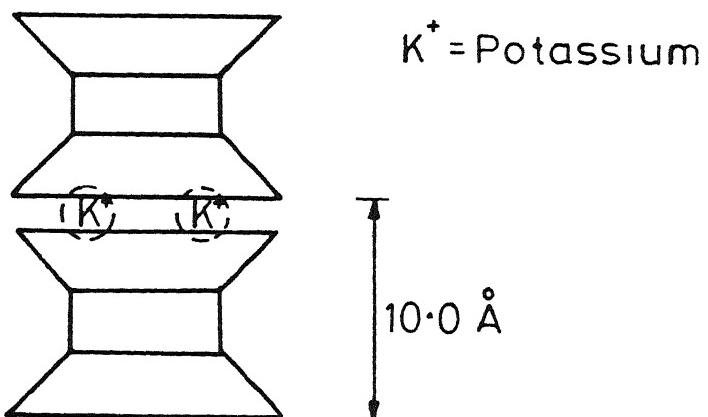
of the 'O' layer are common with oxygen corners of the two 'T' layers on either side. The basic structural formula of the three layer sheet silicate is, therefore, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. In illite, there is a partial substitution of Si^{+4} by Al^{+3} in 'T' layer and the charge deficiency is compensated by K^+ ions in the inter layer position (Fig. 2.2b). Illite can be considered as K-deficient muscovite mica because in muscovite, one out of four Si^{+4} is replaced by Al^{+3} with the formula $\text{K Al}_2(\text{Al, Si}_3)\text{O}_{10}(\text{OH})_2$. On the other hand, the general formula for illite group is $\text{K}_{1-x}\text{Al}_2(\text{Al}_{1-x}, \text{Si}_{3+x})\text{O}_{10}(\text{OH})_2$. The basal spacing of illite and muscovite is 10 \AA . Montmorillonite, on the other hand, shows partial substitution in both 'T' and 'O' layers in varying proportions and the charge deficiency is compensated by Na^+ or Ca^{+2} ions present in the interlayer position. It is also common to find water molecules in the interlayer (Fig. 2.2c). The typical formula of a Na-montmorillonite is $\text{Na}_{0.33}\text{Al}_2(\text{Al}_{0.33}, \text{Si}_{3.67})\text{O}_{10}(\text{OH})_2$. The minimum 'C' axis spacing is 9.2 \AA . However, as a result of sorbed water between the layers, basal spacing can be quite variable. Montmorillonite also shows the property of lattice expansion due to adsorption of inorganic and organic polar molecules.

(v) Size and Shape

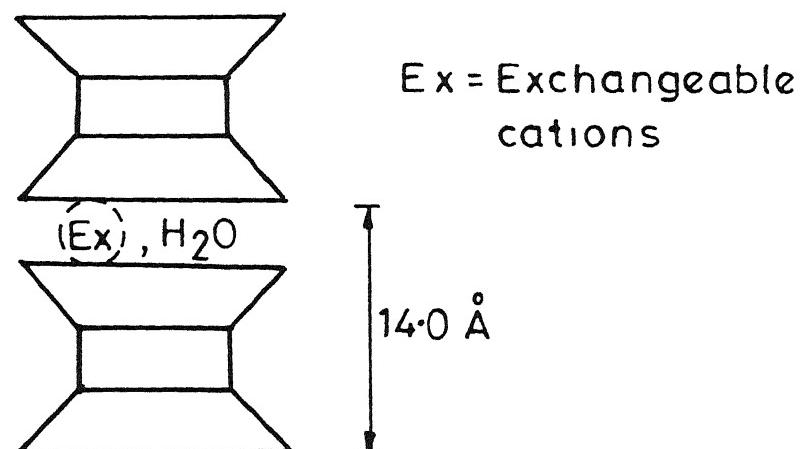
Although the general shape of the clay minerals is flaky, the exact grain size and perfection of shape would



(a) Kaolinite



(b) Illite



(c) Montmorillonite

Fig. 2.2 Schematic representation of the structure of kaolinite, illite and montmorillonite.
After Lambe and Whitman, 1967.

depend upon the degree of crystallinity and other environmental parameters (Wayman, 1967). The following summary of the three principal clay minerals, kaolinite, montmorillonite and illite has been adopted from Grim (1967).

The shape of kaolinite, shown by electron micrographs, ranges from well crystallised hexagonal shaped grains to an irregular mass displaying poor crystalline outline. The surface dimension of the flake surface ranges from 0.3 to 4μ (Micron). The thickness of the individual flakes varies from 0.05 to 2μ .

The electron micrograph of montmorillonite, commonly shows that the individual particles can barely be discerned and are too small to reveal any characteristic outline. Micrographs of some particles show that they are irregular flake shaped aggregate which appear to be stacking of unit without regular outline. The surface dimension of the flake surface ranges from 0.2 to 2μ . The thickness of the individual flakes is in the range of 0.002μ .

The electron micrograph of illite shows poorly defined flakes commonly grouped together in irregular aggregates. The surface dimension of the flake surface ranges from 0.1 to 0.3μ and the minimum thickness of the individual flake is 30\AA .

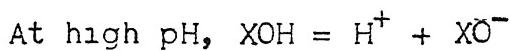
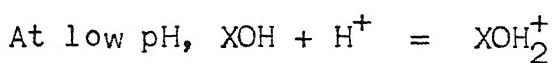
(vi) Exchange Properties

The clay minerals have the property of exchanging anions and cations with water at the clay-liquid interface. The exchangeable ions are held around the outside of the Silica-Alumina structural unit and the exchange reaction generally does not affect the silicate structure (Grim, 1967). The capacity of ion exchange is measured in a unit of milliequivalent of ion per 100 grams of clay. More information is available regarding exchange of cations primarily because clay particles are negatively charged in aqueous suspension. In precise work, cation exchange capacity (CEC) is expressed as milliequivalent per 100 grams at pH 7. The main factors leading to CEC are (1) unsatisfied charges produced by broken bonds at surfaces and edges of the particles (2) unbalanced charges caused by isomorphous substitution of cations, for example, Si^{+4} by Al^{+3} (3) lattice defects, (Carroll, 1959). Among the clay minerals commonly present in soils and sediments, montmorillonite shows highest CEC value of 80-150 me/100 g and kaolinite the lowest value of 3-15 me/ 100 g . This difference is due to the nature of exchange sites in the clay lattice. In kaolinite, broken bonds are the main cause for CEC where as in montmorillonite around 20% of CEC is due to broken bonds and the rest is due to interlayer site (Grim, 1967). Moreover, the total specific surface area of montmorillonite is in the range of $700-800 \times 10^3 \text{ m}^2/\text{Kg}$ compared with much lower value of

$15-40 \times 10^3 \text{ m}^2/\text{Kg}$ for kaolinite (Yariv and Cross, 1979).

Therefore, montmorillonite has larger number of sites for CEC. The CEC of illite is in between the values of kaolinite and montmorillonite.

Although, theoretically, the anion exchange capacity (AEC) can be treated in a manner similar to CEC, interpretation of anion uptake is much more difficult because of the possibility of decomposition of clay structure. Most theories about anion exchange have been associated with adsorption of phosphate (phosphate fixation) by soils. According to Grim (1967) there has been a considerable argument as to whether adsorption of phosphate by kaolinite involves (1) replacement of OH ions by phosphate ions or (2) a reaction between phosphate and alumina produced by the destruction of kaolinite lattice. Another mechanism proposed is the similarity of the size and geometry of SiO_4 tetrahedron and the PO_4^{3-} molecule. A third manner of anion exchange has been attributed to active anion exchange spots on the basal plane due to unbalanced charges. More recently, Stumm and Morgan (1970), and Morel (1983) have proposed a process of pH dependent ionization of the functional groups at the clay surface for anion uptake. Thus at pH values below the zero point of charge (ZPC) the surface is positively charged and the charge becomes negative at higher pH.



Therefore, AEC is more prominent at low pH and CEC increases with increasing pH.

In summary, both CEC and AEC of clay minerals show distinct ranges whereas the order of magnitude may be characteristic of the clay type. Grim (1967), reports the average ratio of CEC to AEC as 0.5 for kaolinite, 2.3 for illite and 6.7 for montmorillonite. The values calculated from these data have been shown in Table 2.1. It is also reported (Grim, 1967) that phosphate fixation by Indian soils show a higher value for montmorillonite when compared with kaolinite and this could be due to exchangeable Ca^{++} in montmorillonite.

The exchangeable ions retained by clay minerals are subjected to two types of attractive forces (1) weak van der Waals force where the ions are easily desorbed (2) stronger attractive force causing chemisorption of ion on the clay mineral structure. Therefore, an adsorption- desorption experiment can distinguish the two processes.

(vii) Clay Colloid

The atomic structure of clay minerals and their ion exchange properties are inter-related through the behavior of clay suspensions as a sol or colloidal suspension . Majority of the clay flakes have thickness in the colloidal range (10^{-3} to 10^{-6} mm i.e. 1 μm to 1 nm) whereas, the particle may exceed the upper limit of colloidal size. Some important properties like surface charge, exchange and adsorption of ions from solution, Brownian movement, flocculation by electrolytes are all typical of colloid behaviour (Krauskopf, 1979).

Table 2.1 Calculated range of CEC and AEC of clay mineral (Source; Grim, 1967)

Clay mineral	CEC in me/l	AEC in me/l	CEC / AEC
1. Kaolinite	3-15	6.6-20.2	0.5
2. Illite	10-40	4.3-17.4	2.3
3. Montmorillonite	80-150	23-31	6.7

A net negative charge on clay colloids can be demonstrated by migration of particles towards a positive electrode. On the other hand, there is a considerable evidence to support that two types of charges exist on a clay particle (Fig. 2.3). The flat surfaces have a negative charge whereas the particle edges have both positive and negative sites (Wayman, 1967). Clear support for positively charged particle edges comes from electron micrographs showing negative gold particles adsorbed along the edges of kaolinite flakes (Van Olphen, 1977). As the area of the flat surface is much larger than the edges, the net charge on the particle is negative.

The main reason for a deficiency of positive charge on the flat surface is isomorphous replacement of Si^{+4} by Al^{+3} in the T-layer or Al^{+3} by Mg^{+2} in the O-layer. On the other hand, at the edge of the particles, the T and O layers are disrupted. Broken bonds like $\text{Si}-\text{O}-\text{Si}$ or $\text{Al}-\text{O}-\text{Al}$ create a positive charge whereas $\text{Si}-\text{O}-\text{Si}-\text{O}$ or $\text{Al}-\text{O}-\text{Al}-\text{O}$ would give rise to negatively charged sites.

In a clay sol, the particle charges are internally compensated by the development of an electric double layer (Van Olphen, 1977). This double layer consists of the charged particle surface surrounded by a diffuse layer of counter ions of opposite charge (Fig. 2.4). Thus the flat surface will have a double layer with the diffuse layer of positive ions whereas the particle edges may have a double layer with the diffuse layer of negative ions. The concentration of counter ions gradually

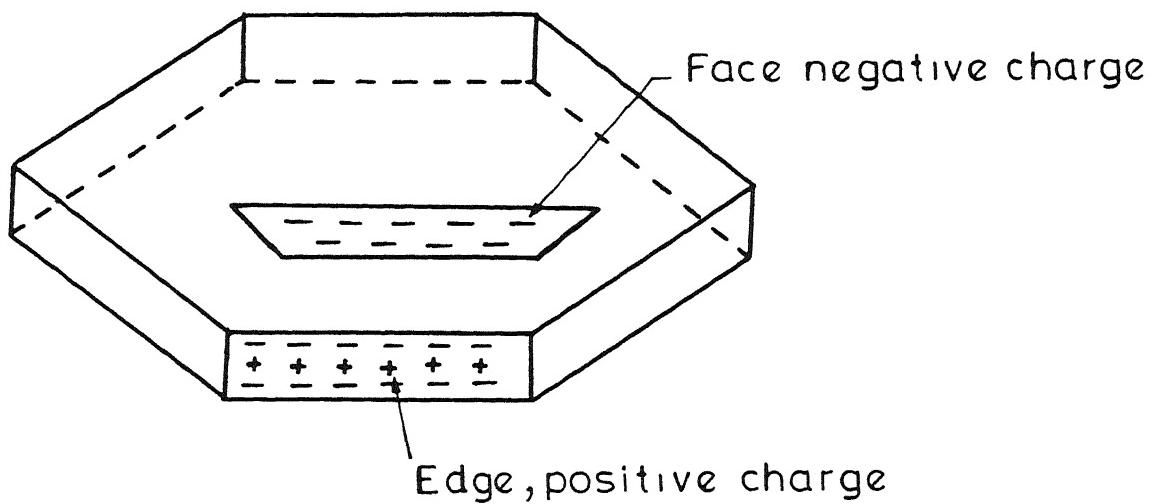


Fig. 2.3 Sketch of dual charge on a kaolinite particle. (Source: Jayman, 1967).

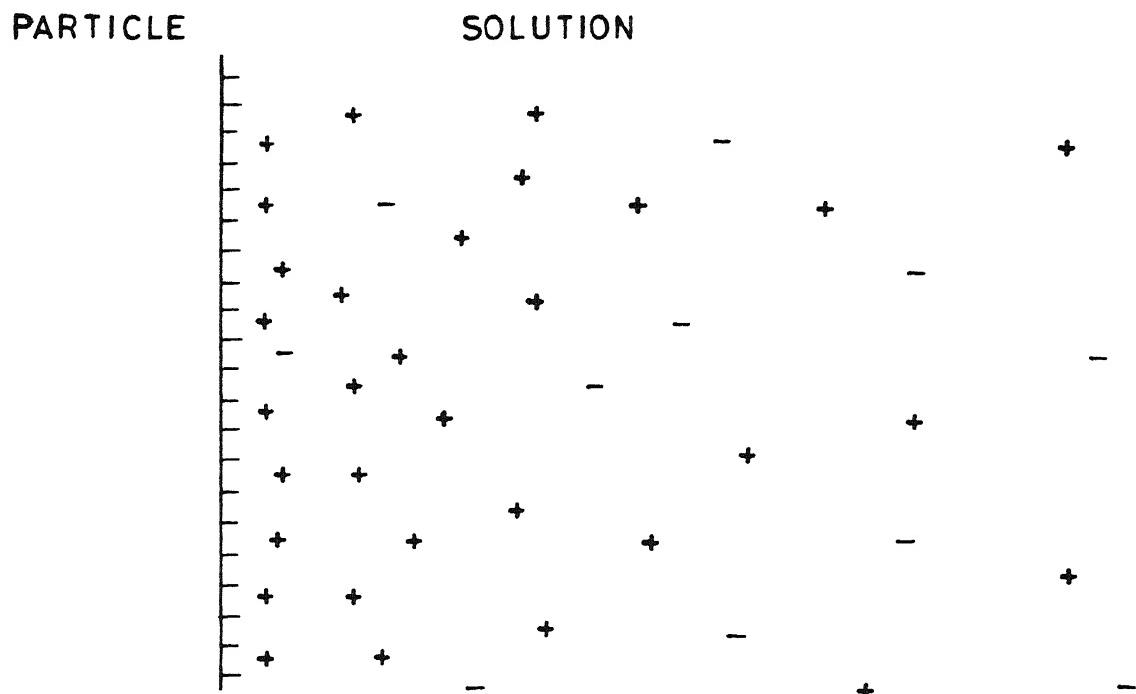


Fig. 2.4 Diffuse electric double layer.
(Source : Van Olphen, 1977, Page 30).

decreases away from the clay-water interface.

In a salt free suspension of clay in water, there are two types of forces acting on the surface (1) repulsive forces between similar charged particles and (2) attractive (van der Waals) forces between the particles. However, the existence of Brownian movement proves that repulsive forces are stronger. When an electrolyte is added, oppositely charged ions from the solution compress the double layer and attractive forces slowly overcome the repulsive forces. Therefore, when two particles collide, they stick to each other and create a larger sized particle or 'floc'. The flocculation power of an electrolyte obeys the Schulz-Hardy law i.e. the higher the valence of the ion, greater the flocculating power. Thus an Al salt has more flocculating power than a Ca or Na salt. When a suspension of plate like clay particles of flocculate, three different modes of particle association may occur: face to face (FF), edge to face (EF) and edge to edge (EE) as shown in (Fig. 2.5). The FF association merely leads to thicker and possibly larger flakes which is known as association. On the other hand, EE and EF associations will lead to a three dimensional, voluminous card-house structure causing flocculation. The dissociation of FF association is called dispersion whereas that of EE and EF association are called deflocculation (Van Olphen, 1967). The major natural counter part of flocculation by salt is found at river mouth, when in the upper estuary, flocculation of suspended clay leads to sedimentation. Observation of mud balls

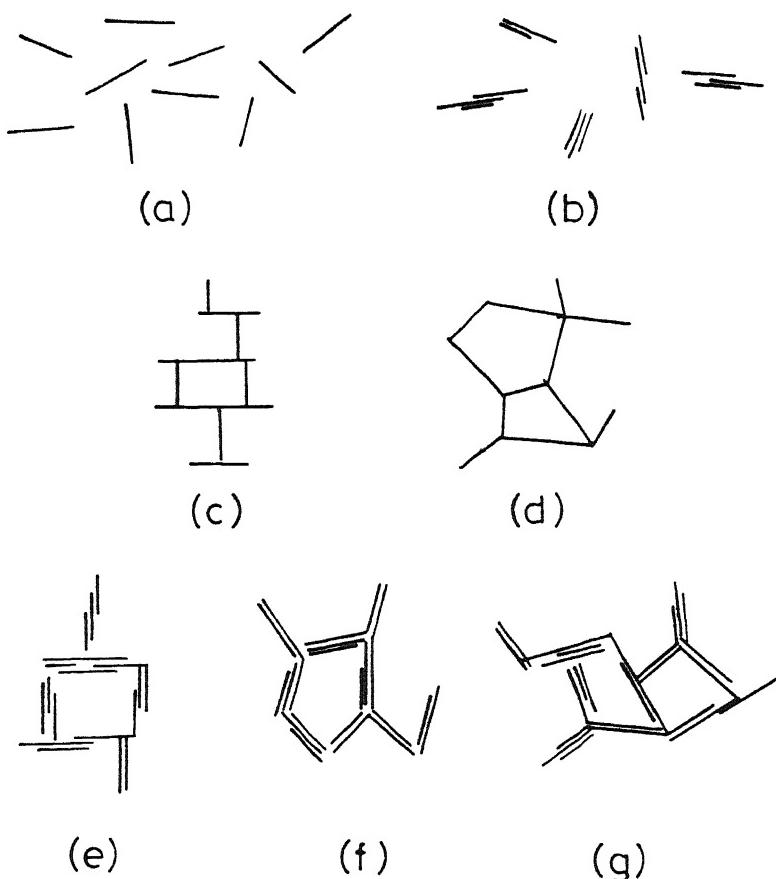
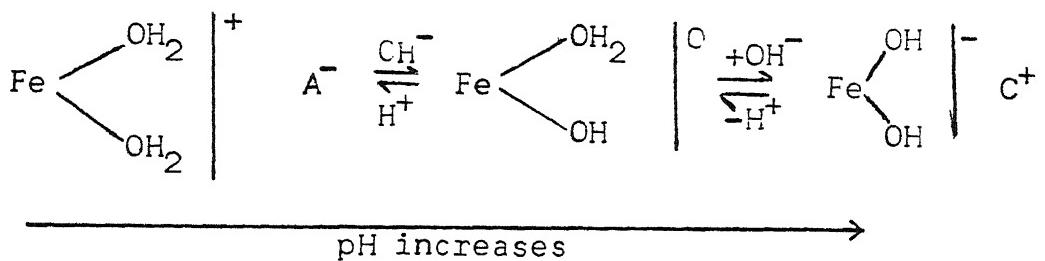


Fig. 2.5 Modes of particle association in clay suspensions and terminology. (a) "Dispersed and deflocculated" (b) Aggregated but deflocculated (face to face association) (c) Edge to face, flocculated but "dispersed" (d) Edge-to-Edge, flocculated but dispersed" (e) Edge-to-face, flocculated and "aggregated" (f) Edge-to-edge, flocculated and aggregated" (g) Edge to face and edge-to-edge, flocculated and "aggregated". (Source: Van Olphen, 1977, Page 97).

on tidal flat on the Orissa coast is an example of this process (Raymahashay, 1971). When clay minerals (kaolinite, illite and montmorillonite) that are carried in colloidal suspension in river water, encounter greater salinity of sea water, the concentration of the ions in the water between the particles increases. This brings about a thinning or collapsing of the double layer so that the charged particle may come together thus leading to flocculation. The stability of clay suspension when subjected to saline water is not only dependent on the salinity of water but also on the type of clay involved (Berner and Berner, 1987).

Role of Iron Oxide

Since PO_4^{3-} is a negative radical it is fixed on the positive site on clays and iron oxide colloids present in soils and weathered rocks. Schwertmann and Taylor (1977) have explained that the surface of iron oxide in aqueous solution gets charged due to adsorption of either H^+ or OH^- ions from the solution. So the charge of the iron oxide will depend upon pH of the solution in the following way.



An excess of positive or negative charge at the surface is balanced by an equivalent amounts of anions (A^-)

or cations (C^+) either by nonspecific adsorption or by specific adsorption or both. In the first case, anions like Cl^- , NO_3^{-4} , ClO_4^- and cations (mostly the alkali and alkaline earth) are held electrostatically on the outer diffuse electric double layer. On the other hand, in specific adsorption anions (e.g. PO_4^{-3}) or other cations penetrate the coordination shell of the Fe-atom and exchange their OH and OH_2 ligands and are bonded by covalent bonds directly via their O and OH groups to the structural cation. The role of iron oxide on adsorption was further explained by Mehta (1982), who found out that lateritic soils which contained a mixture of clay minerals and iron oxide were the most efficient for phosphate fixation.

CHAPTER 3

MATERIALS AND METHODS

The major components of the experiments were (1) clay minerals and natural soils to represent suspended load in river and (2) phosphate solutions of known concentration with and without a NaCl fraction to represent fresh river water and upper estuary. Some details about these are given below.

Clay Minerals and Soils

Two commercial kaolinite samples, one sample of lateritic soil from Kerala and another sample of black cotton soil from Maharashtra were used in the experiments.

Kaolinite -I was obtained from the Geotechnical Engineering Laboratory, IIT Kanpur. The X-ray diffraction pattern (Fig. 3.1). showed it was of poor quality. There were almost equal proportions of kaolinite and illite along with traces of quartz and feldspar.

Kaolinite -II was obtained from the Engineering Geology Laboratory, IIT Kanpur. Its X-ray pattern (Fig.3.2) indicated better quality with sharp and strong peaks of kaolinite with traces of illite and quartz.

The lateritic soil was taken from the collection by Kirkos (1986). It came from the Calicut area of Kerala. It had developed over charnockite and biotite gneiss bed rock. Its X-ray pattern (Fig. 3.3) showed peaks of kaolinite,

KAOLINITE-I

F - Feldspar
II - Illite
K - Kaolinite
Q - Quartz

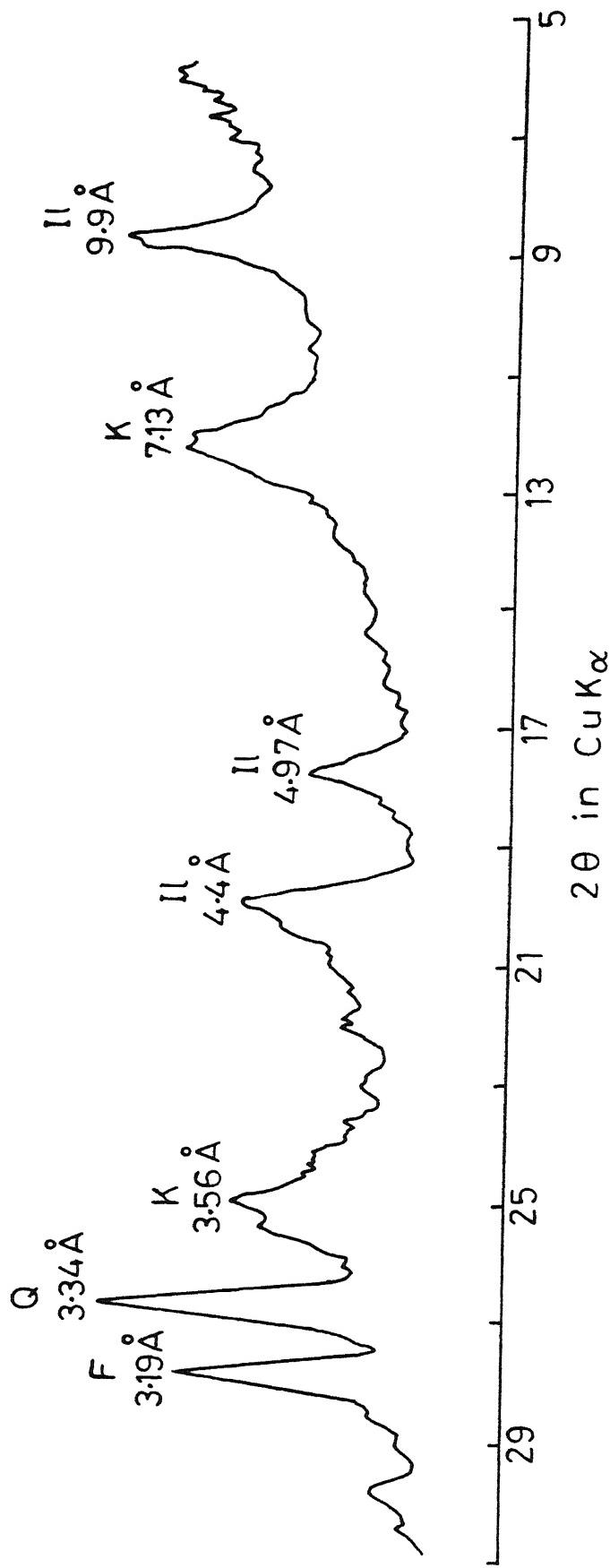


Fig. 3.1 γ -ray Diffraction Pattern of Kaolinite-I

KAOLINITE-II

K
7.18 Å

K - Kaolinite

II - Illite

Q - Quartz

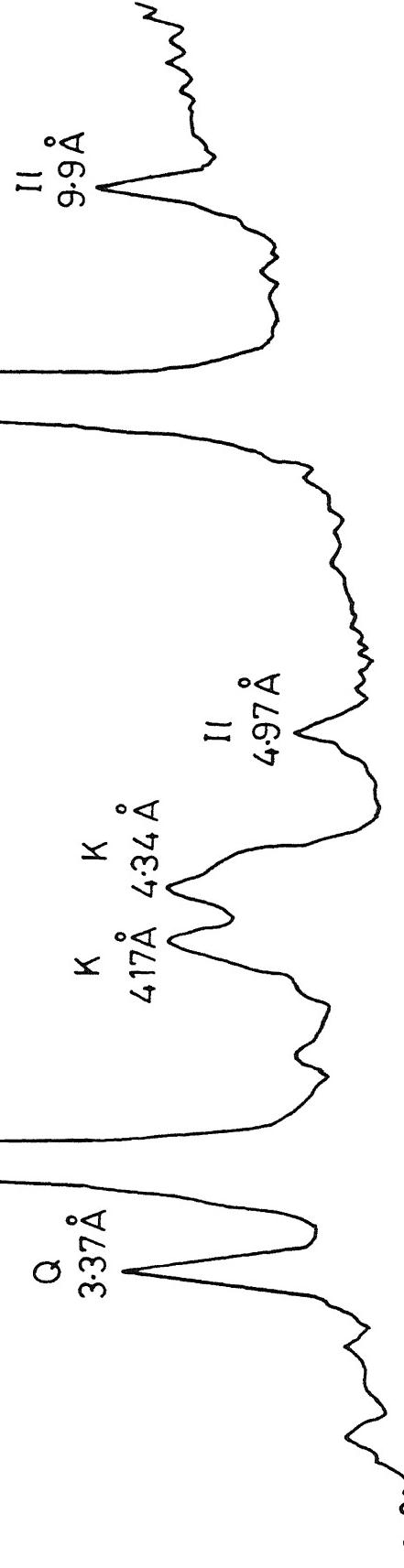
K
3.57 Å

Q
3.37 Å

K
4.17 Å

K
4.34 Å

II
4.97 Å



2θ in $\text{CuK}\alpha$

Fig. 1. X-ray, Diffraction, Pattern of Kaolinite-II

LATERITIC SOIL

K - Kaolinite

G - Gibbsite

Go - Goethite

Q - Quartz

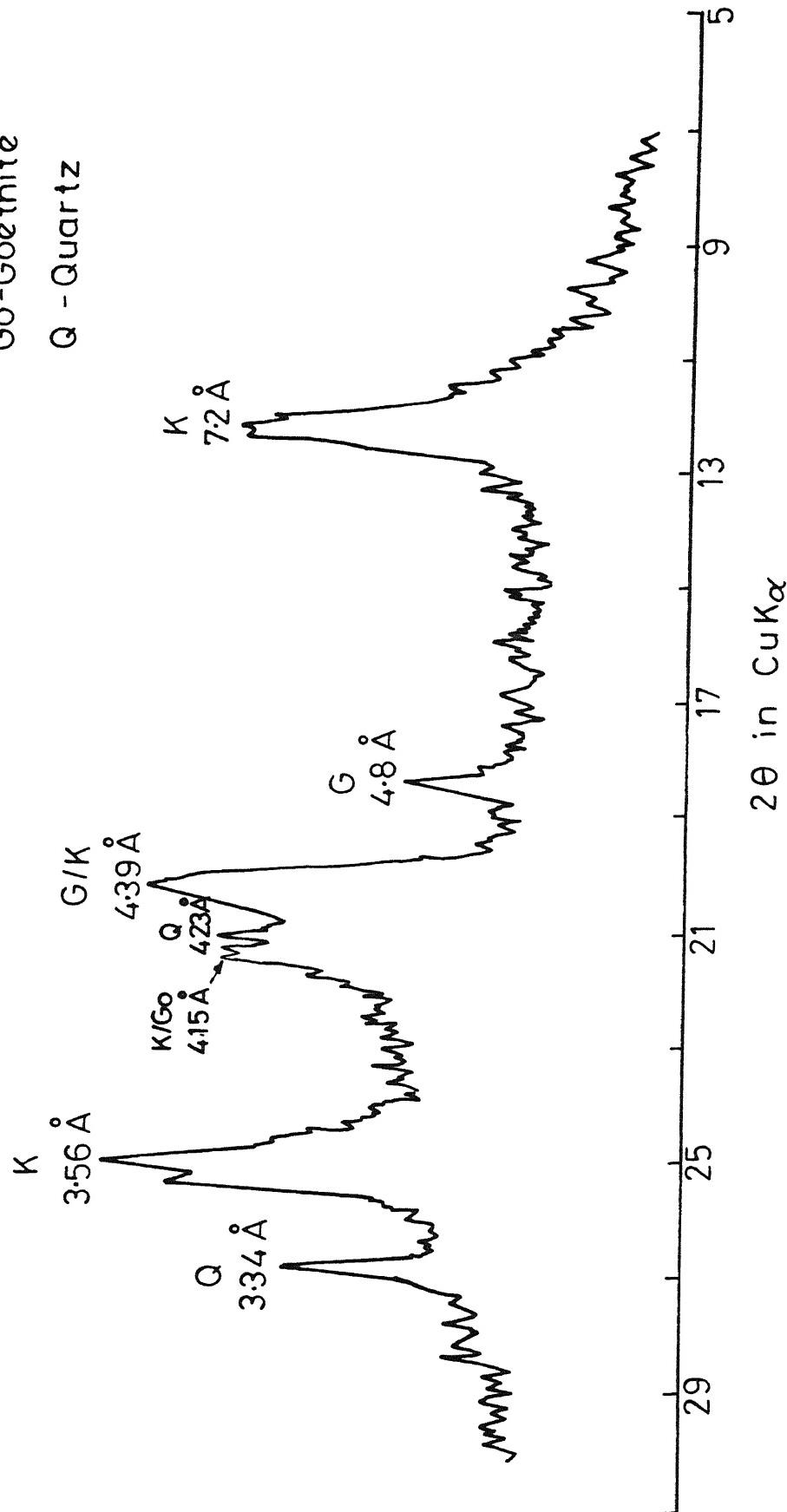


Fig. 2.3 X-ray Diffraction Pattern of Lateritic Soil
(Source: Kirkpatrick, 1996).

gibbsite, goethite and quartz. The red colour was obviously due to iron oxide/hydroxide. However, as only one X-ray peak of goethite was seen it was concluded that most of the iron occurred as X-ray amorphous forms (limonite). Other properties of this soil determined by Kirkos (1986) were: depth below surface = 1.9 m, clay fraction = 13.7%, organic matter = 7.5%, soil pH = 7.3 and CEC = 9.6 me/100 g.

The black cotton soil was also collected by Kirkos (1986) from the Pune area of Maharashtra. It had developed over Deccan basalt. Its X-ray pattern (Fig. 3.4) showed mainly montmorillonite and traces of unweathered feldspar. Montmorillonite was confirmed by glycolation test when the 14.96°A basal peak shifted to 16.7°A . Other properties of this soil were: depth below surface = 0.9 m, clay fraction = 20%, organic matter = 9.6%, soil pH = 8.1 and CEC = 83 me/100 g.

Phosphate Solution

Four types of phosphate solutions were used in the experiments. These were (1) Acidified 5 mg/l (2) Acidified 2 mg/l (3) Normal 2 mg/l and (4) 2 mg/l in NaCl- NaHCO_3 buffer.

A phosphate stock solution of 500 mg/l concentration was prepared by dissolving 0.18 g of analytical grade potassium dihydrogen phosphate (KH_2PO_4) in 250 ml of distilled water. 5 mg/l and 2 mg/l solutions were prepared by appropriate dilution of this stock solution. The solutions were 'acidified' when pH was lowered by arbitrary mixing with HCl. Without HCl

BLACK COTTON SOIL

F - Feldspar

M - Montmorillonite

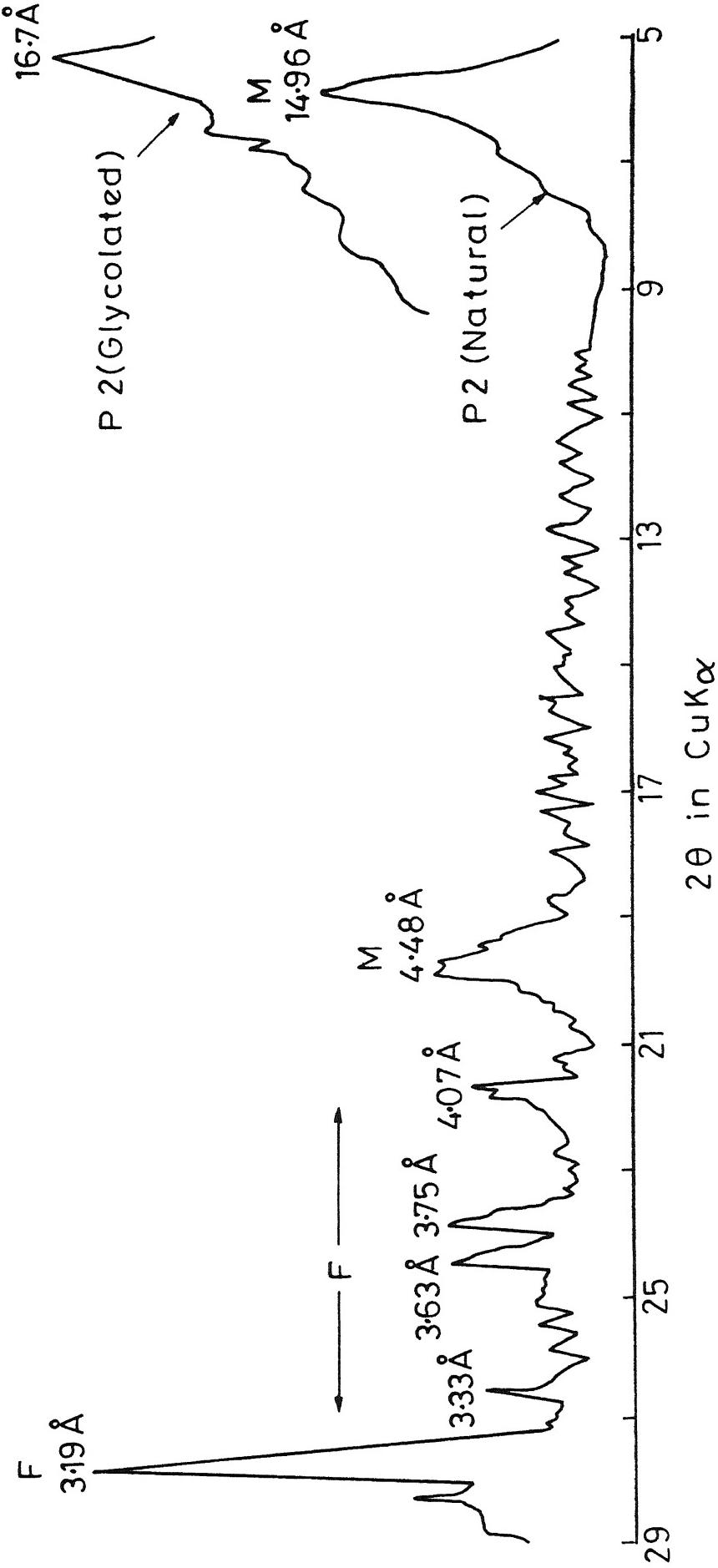


Fig. 3.1

X-ray Diffraction Pattern of Black Cotton Soil
(Source: Kirton, 1961).

treatment, the solution was called 'normal'. These two types of solutions were used to study the effect of acidic pH on adsorption of negatively charged anionic phosphate species.

The purpose of using NaCl-NaHCO₃ buffered phosphate solution was to simulate the mixing zone between river and sea in the upper estuary. The procedure of Edzwald et al. (1974) was slightly modified. In 100 ml of 2 mg/l normal phosphate solution, 1.74 g of analytical grade NaCl and 0.05 g of analytical grade NaHCO₃ were dissolved. The molar concentration of this solution is given in column a of Table 3.1. The pH of the solution was buffered at a value of 8.37. In subsequent experiments pH was buffered at two other values (1) 8.01, by dissolving 1.74 g of NaCl and 0.03 g of NaHCO₃, (2) 8.13 by dissolving 1.75g of NaCl and 0.03 g of NaHCO₃. The molar concentrations of these solutions are given in column b and c of Table 3.1. These three pH values cover the range expected in the mixing zone between river and sea in the upper estuary. The ionic strength of these solutions calculated from the formula $I = \frac{1}{2} \sum m_i z_i^2$, averaged around 0.30. It should be noted that the average pH and ionic strength of open sea water are 8.1 and 0.7 respectively. In other words, the chlorinity of three solutions ranged between 0.29 moles/l (10,579 mg/l) and 10,615 mg/l which is much below the average chloride content of 19,000 mg/l in sea water. The HCO₃ concentration is slightly higher than average sea water value of 120 mg/l but may cover the linity of polluted estuaries. These, experiments has therefoi , been performed in solutions representing the low salinity upper estuary zone.

Table 3.1 Calculated Ion Concentration (moles/l) in salt
Solutions used in Experiments.

Species	Solution(a)	Solution(b)	Solution(c)
Na ⁺	0.303	0.301	0.302
HCO ₃	5.95×10^{-3} (363 mg/l)	3.57×10^{-3} (217 mg/l)	3.57×10^{-3} (217 mg/l)
Cl ⁻	0.298 (10,579 mg/l)	0.298 (10,579 mg/l)	0.299 (10,615 mg/l)
PO ₄ ⁻³	0.0000013	0.0000013	0.0000013
H ⁺	0.0000013	0.0000013	0.0000013
K ⁺	0.0000013	0.0000013	0.0000013
Ionic Strength	0.3000375	0.3017925	0.3017935
pH	8.37	8.01	8.13

Apparatus Used

The following apparatus were used to carry out the experiments.

1. Type 'XL' Servall Angle Centrifuge (Ivan Sorvall Inc., U.S.A.).
2. Systronics type 335 digital pH meter (Systronics, Naroda, India).
3. Systronics 103 Spectro Colorimeter (Systronics, Naroda, India).
4. K-12 (Super) Analytical Single Pan Balance (K.Roy and Co., Varanasi, India).
5. Hot Air Oven (Adair Dutt and Co., Calcutta, India).
6. Type 2LH, Magnetic Stirrer (Remi Corporation, India).
7. DEBYEFLEX 2002 (Automatic Powder X-ray diffractometer, Seifert and Co., U.S.A.).
8. Standard Laboratory Glassware.

Phosphate Analysis

Total orthophosphate in solution was determined by the colorimetric stannous chloride method using an acid ammonium molybdate reagent (Standard Methods, 1965). The basic principle is to form an ammonium phospho-molybdate complex which is reduced by SnCl_2 to give a blue coloured solution. The intensity of blue colour is proportional to phosphate concentration. Calibration curves were prepared by using phosphate standards and transmission was measured at 690 nm in a Spectro-Colorimeter. A linear

relationship was obtained between log T and mg/l phosphate.

A typical calibration curve is shown in Fig. 3.5 . Reagent blanks were run and samples were diluted when required. The accuracy of this method is of the order of 2 percent.

Adsorption Experiment

The samples were sieved in the size range -240,+350 (0.045 to 0.065 mm) or -200,+240 (0.065 to 0.075 mm) depending upon the initial coarseness. Weighed amounts of clay or soil was stirred into phosphate solution of pre-determined composition so as to give an 1% suspension. After an equilibrium time of 18 to 24 hours, the suspension was first filtered through Whatman 42 filter paper and the filtrate was further centrifuged for 10 to 30 minutes at 800 to 1900 rpm depending on the turbidity. Final pH and phosphate were determined in the clear solution. Phosphate adsorption was calculated by the difference between initial and final concentration. It was generally observed that turbidity was less in NaCl suspensions.

Desorption Experiments

The clay or soil filtered from the adsorption experiment was washed free of phosphate solution adhering to the particles by testing the washings with ammonium molybdate reagent and SnCl_2 . It was then oven dried and weighed. The sample was re-dispersed into measured volumes of distilled

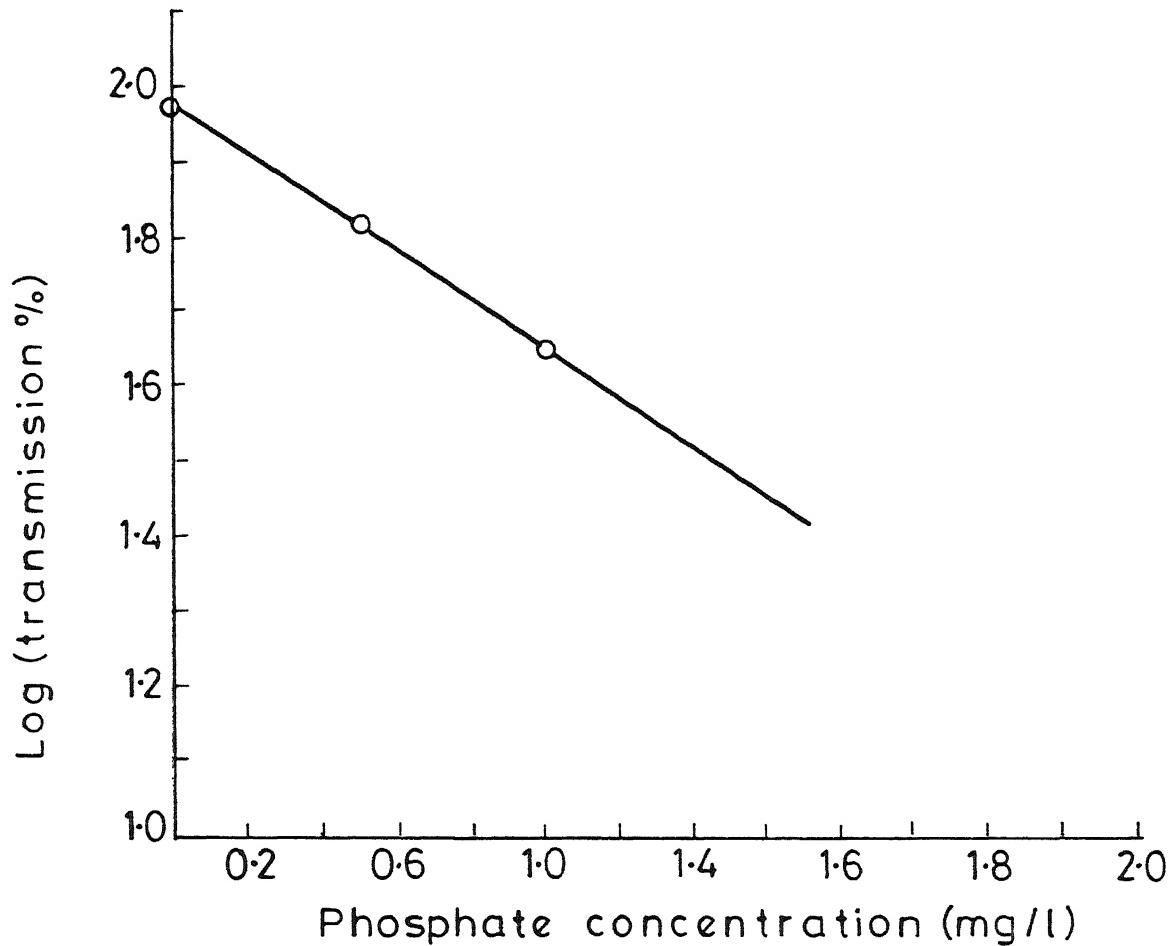


Fig. 3.5 A typical calibration curve for phosphate analysis.

water or NaCl - NaHCO₃ solution to give an 1% suspension. After a contact time of 24 hours, the suspension was filtered and centrifuged. Final phosphate was determined in the clear solution. Phosphate desorption was calculated by expressing the amount released as a fraction of the amount adsorbed.

CHAPTER 4

RESULTS AND DISCUSSION

Some important experimental parameters of this work were provided by the earlier investigation by Mehta (1982). He concluded that at room temperature lateritic soil was capable of complete removal of phosphate from solutions having relatively low initial concentration (P_i). The efficiency of removal increased in acidified solution. It was also noted that phosphate uptake by kaolinite clay was less efficient compared with lateritic soil.

Based on the above observations the first few experimental runs were carried out with commercial kaolinite and natural lateritic soil. Mehta's work was extended by determining desorption in both cases and by conducting adsorption-desorption experiments in phosphate-NaCl-NaHCO₃ buffer solutions. Finally similar experiments were carried out with black cotton soil. The clay/soil suspension was maintained at 1% to represent low turbidity river water. The room temperature varied from 13.5 to 32°C during the course of the experiments.

Table 4.1 summarises the results of phosphate adsorption from acidified 5 mg/l solution by kaolinite-I and kaolinite-II. It was purer in quality had a phosphate adsorption capacity two times that of kaolinite-I, other

Table 4.1 Phosphate Adsorption by kaolinite from acidified 5 mg/l solutions. Grain size = -240 +350 sieve (0.045 mm to 0.065 mm) and suspension = 1%

Clay	Temp (°C)	Contact time (hours)	pH _i	pH _f	P _f (mg/l)	Adsorp- tion (%)
• Kaolinite-I	20	18	2.85	5.79	4.4	12
• Kaolinite-II	20	18	2.85	6.8	3.8	24
• Kaolinite-II	13.5	24	2.85	6.9	3.65	27

Table 4.2 Phosphate adsorption by kaolinite II from 2 mg/l solutions. Grain size = -240 +350 sieve (0.045 to 0.065 mm), suspension = 1%, contact time = 24 hours.

P _i	Temp (°C)	pH _i	pH _f	P _f (mg/l)	Adsorp- tion (%)	Desorption in disti- lled water
• 2 mg/l Acidified	20	3.15	7.57	1.29	35.5	0.26/0.71 = 36%
• 2 mg/l Normal	18	6.16	7.36	1.70	15	0.1/0.3 = 33.3%
• 2 mg/l in NaCl-NaHCO ₃ ^(a)	21.5	8.37	8.67	1.93	3.7	Turbid

(a): Solution (a) in Table 3.1, Chapter 3.

pH_i = Initial pH

pH_f = Final pH

P_i = Initial phosphate concentration

P_f = Final phosphate concentration

Temp = Temperature

parameters remaining same. Phosphate adsorption increased further when contact time increased from 18 to 24 hours. Mehta (1982) also reported that the equilibrium was achieved within 24 hours. Therefore, contact time was kept constant at 24 hours for all further experiments.

Table 4.2 shows the effect of lowering initial PO_4 concentration to 2 mg/l. It is clear that adsorption from acidified 2 mg/l phosphate solution was higher than that from acidified 5 mg/l phosphate solution for the same contact time. On the other hand, adsorption decreased when the initial phosphate solution was not acidified. This is because the population of positively charged site on the clay surface decreases with increasing pH (Morel, 1983).

A new parameter was identified by introducing a $\text{NaCl}-\text{NaHCO}_3$ buffer in the initial phosphate solution. The results indicate that in the presence of 10, 579 mg/l chloride (Ionic strength = 0.30) and pH buffered at 8.37, kaolinite adsorbed much less phosphate compared with distilled water solution of same phosphate concentration. In other words, adsorption in saline water was less than in fresh water. This trend was repeated for the other soils. Detailed explanation for the overall process is given later.

Another new feature of this set of experiments was the study of desorption into distilled water. The results listed in Table 4.2 show that 36% of the phosphate adsorbed from acidified 2 mg/l solution was released by desorption.

Although the adsorption was less from normal phosphate solution, one third of the adsorbed amount was released by desorption. This indicates that only a part of the total phosphate adsorbed is held permanently on the clay surface. The desorption experiments after adsorption from the phosphate-NaCl-NaHCO₃ solution resulted in high turbidity. It was apparent that when the phosphate saturated kaolinite was dispersed in distilled water it continued to remain in suspension although it had settled down in salt solution. This phenomenon was confirmed by a spot experiment. The same fine grained kaolinite was suspended in NaCl solution to give flocculation. It was filtered and re-dispersed in distilled water. After 24 hours the superntant was turbid. This problem was overcome in later experiments by taking coarser size of soil and increasing the centrifuge time and speed.

For application to real life situations the behaviour of natural soil is more important than pure clays. Therefore, after establishing the experimental parameters with kaolinite clay further investigations was carried out with lateritic and black cotton soil. The results have been summarised in Table 4.3. It was observed that the lateritic soil showed 100% phosphate adsorption from 2 mg/l solution. This is in agreement with the result reported by Mehta (1982). Moreover, the phosphate was permanently held as there was no desorption. On the other hand, in the salt solution having ionic strength =0.3 and pH=8.13, adsorption was less (91%) and there was 9% desorption. However, the adsorption value was much higher compared with kaolinite under similar condition. This difference between kaolinite and laterite can be attributed to the presence of positively charged iron

Table 4.3 Phosphate adsorption-desorption by lateritic and black

cotton soil. Grain size = - 200 +240 sieve (0.065 to
0.075 mm), suspension = 1%, contact time 24 hours.

Soil	Initial PO_4 concentra- tion	Temper- ature ($^{\circ}\text{C}$)	Initial pH	Final pH	Final PO_4 Concen- tration (mg/l)	Adsor- ption (%)	Desorption
1. Lateritic	2 mg/l Normal	32	6.16	6.27	0.0	100	0.0 in distilled water
2. Lateritic	2 mg/l in NaCl^{-} NaHCO_3^{-} (c)	28	8.13	7.96	0.18	91	0.18/1.82 = 9% in distilled water
3. Black Cotton Soil	2 mg/l Normal	28	6.16	7.40	1.15	42.5	0.14/0.85 = 16.4% in distilled water
4. Black Cotton Soil	2 mg/l in NaCl^{-} NaHCO_3^{-} (b)	25	8.01	8.36	1.81	9.5	0.02/0.19 = 10.5% in distilled water
5. Black Cotton Soil	2 mg/l Normal	30	6.16	7.89	1.10	45	0.32/0.9 = 35.5% in $\text{NaCl}-\text{NaHCO}_3$
6. Black Cotton Soil	5 mg/l Normal	30	6.78	7.73	4.75	5	0.13/0.25 = 52% in distilled water

(b) : Solution (b) in Table 3.1, Chapter 3

(c) : Solution (c) in Table 3.1, Chapter 3

(d) : NaCl and NaHCO_3 same as solution (a) in Table 3.1, Chapter 3 but with no phosphate.

oxide colloids in lateritic soil (Schwertman and Taylor, 1977).

The black cotton soil dominated by montmorillonite clay showed phosphate adsorption lower than laterite but higher than kaolinite in normal and salt solution. Desorption in distilled water was more than lateritic soil and lower than kaolinite. Another variation was introduced in the desorption experiment by dispersing the phosphate saturated black cotton soil in a buffered NaCl solution of ionic strength 0.30 . For this purpose, 0.87 g of NaCl and 0.025 g of NaHCO_3 were dissolved in 50 ml. of distilled water. It was observed that in the presence of 10,579 mg/l Cl , the percentage of desorption was more than that in distilled water whereas adsorption from normal 2 mg/l phosphate solutions (expt.3 and 5 Table 4.3) matched within experimental error in the two cases. The last experiment with black cotton soil consisted of adsorption-desorption from normal 5 mg/l phosphate solution. In a trend similar to the kaolinite experiment, adsorption was less compared with 2 mg/l phosphate solution. This system also showed the maximum desorption(52%).

The gross results of these experiments can be summarised as follows.(1) phosphate adsorption from normal 2 mg/l phosphate solution was maximum (100%) for lateritic soil (2) black cotton soil (42.5 to 45%) and kaolinite soil (15%) showed lower adsorption capacity.(3) in artificial upper estuary water of pH around 8 and ionic strength of 0.3, phosphate adsorption was lower for all soils.(4) 33.3% of the phosphate adsorbed by kaolinite and 10.6% of phosphate adsorbed by black cotton soil was desorbed into distilled water. However lateritic

soil showed no desorption. (5) the fraction desorbed increased slightly for all soils when initial adsorption took place in salt solution.(6) desorption from black cotton soil into salt solution was higher than desorption into distilled water.(7) in a trend similar to previous work,phosphate adsorption increased at lower pH and decreased at higher initial phosphate concentration . Some fundamental aspects of these results are discussed below.

Phosphate Level at River Mouth

Table 4.4 compares the average compositions of river and sea water. It is seen that along with major increase in Na^+ and Cl^- , total orthophosphate increases four times from river to sea. The phosphate values in Indian rivers have been listed in Table 4.5 . It is observed that values higher than sea water have been found at the mouth of Ganga, Indus, Mahanadi, Godavari and Cauvery. This is at least partly due to pollution sources like fertilizer run off, paper mills, domestic sewage etc. (Subramanian, 1984). The critical level of phosphate for undesirable algal bloom is around 0.03 mg/l(Sawyer and McCarty, 1978). Therefore, a few mg/l PO_4 is expected to be the upper limit in polluted estuaries. From the point of view of field application and convenience of analysis, the initial phosphate concentration (P_i) was kept at 2 mg/l in most of the experiments in the present investigation.

Distribution of Phosphate Species in Solution

The total dissolved orthophosphate in experimental and natural soil is given by

Table 4.4 Average composition of river and sea water.

Adopted from Berner and Berner (1987). Concentration in mg/l.

	World Average River Water	Average Sea Water of 35 ppt salinity
Cl ⁻	8.3	19, 354
Na ⁺	7.2	10,770
Mg ⁺²	3.7	1, 290
SO ₄ ⁻²	11.5	2, 712
Ca ⁺²	14.7	412
K ⁺	1.4	399
HCO ₃ ⁻	53.0	120 (at pH = 8.1)
SiO ₂	10.2	6.0
Orthophosphate (P _T)	0.07	0.1 (0.01 to 0.28)

Table 4.5 Phosphate concentration in Indian rivers.
From Subramanian (1984).

River	Phosphate mg/l		
	Max	Min	Av
Ganga	0.55	0.02	0.12
Brahmaputra	0.18	0.01	0.12
Indus	0.43	0.0	0.15
Narmada	0.10	0.08	0.09
Tapti	0.12	0.08	0.10
Mahanadi	0.45	0.12	0.18
Godavari	0.62	0.05	0.16
Krishna	0.10	0.05	0.07
Cauvery	0.22	0.01	0.04

Max = Maximum, Min = Minimum , Av = Average.

$$P_T = mPO_4^{-3} + mHPO_4^{-2} + mH_2PO_4^- + mH_3PO_4$$

(Moles/l)

The individual orthophosphate species are related to each other through three dissociation constants. Assuming activity coefficients as unity in dilute solutions,

$$\frac{mHPO_4^{-2}}{mPO_4^{-3} \cdot aH^+} = K_1$$

$$\text{or } mHPO_4^{-2} = K_1 \cdot mPO_4^{-3} \cdot aH^+$$

$$\text{Similarly, } \frac{mH_2PO_4^-}{mHPO_4^{-2} \cdot aH^+} = K_2$$

$$\text{or } mH_2PO_4^- = K_2 \cdot mHPO_4^{-2} \cdot aH^+$$

$$= K_1 \cdot K_2 \cdot mPO_4^{-3} \cdot (aH^+)^2$$

$$\text{and } \frac{mH_3PO_4}{mH_2PO_4^- \cdot aH^+} = K_3$$

$$\text{or, } mH_3PO_4 = K_3 \cdot mH_2PO_4^- \cdot aH^+$$

$$= K_1 \cdot K_2 \cdot K_3 \cdot mPO_4^{-3} \cdot (aH^+)^3$$

Substituting these values,

$$P_T = mPO_4^{-3} [1 + K_1 \cdot aH^+ + K_1 \cdot K_2 \cdot (aH^+)^2 + K_1 \cdot K_2 \cdot K_3 \cdot (aH^+)^3]$$

$$\text{or, } mPO_4^{-3} = \alpha \cdot P_T$$

$$\text{where } \alpha = [1 + K_1 \cdot aH^+ + K_1 \cdot K_2 \cdot (aH^+)^2 + K_1 \cdot K_2 \cdot K_3 \cdot (aH^+)^3]^{-1}$$

The values of K_1 , K_2 and K_3 are $10^{12.4}$, $10^{7.2}$ and $10^{2.1}$ respectively at 25°C (Krauskopf, 1979). Therefore knowing total dissolved phosphate and pH at room temperature, it is possible to calculate the concentration of individual orthophosphate species.

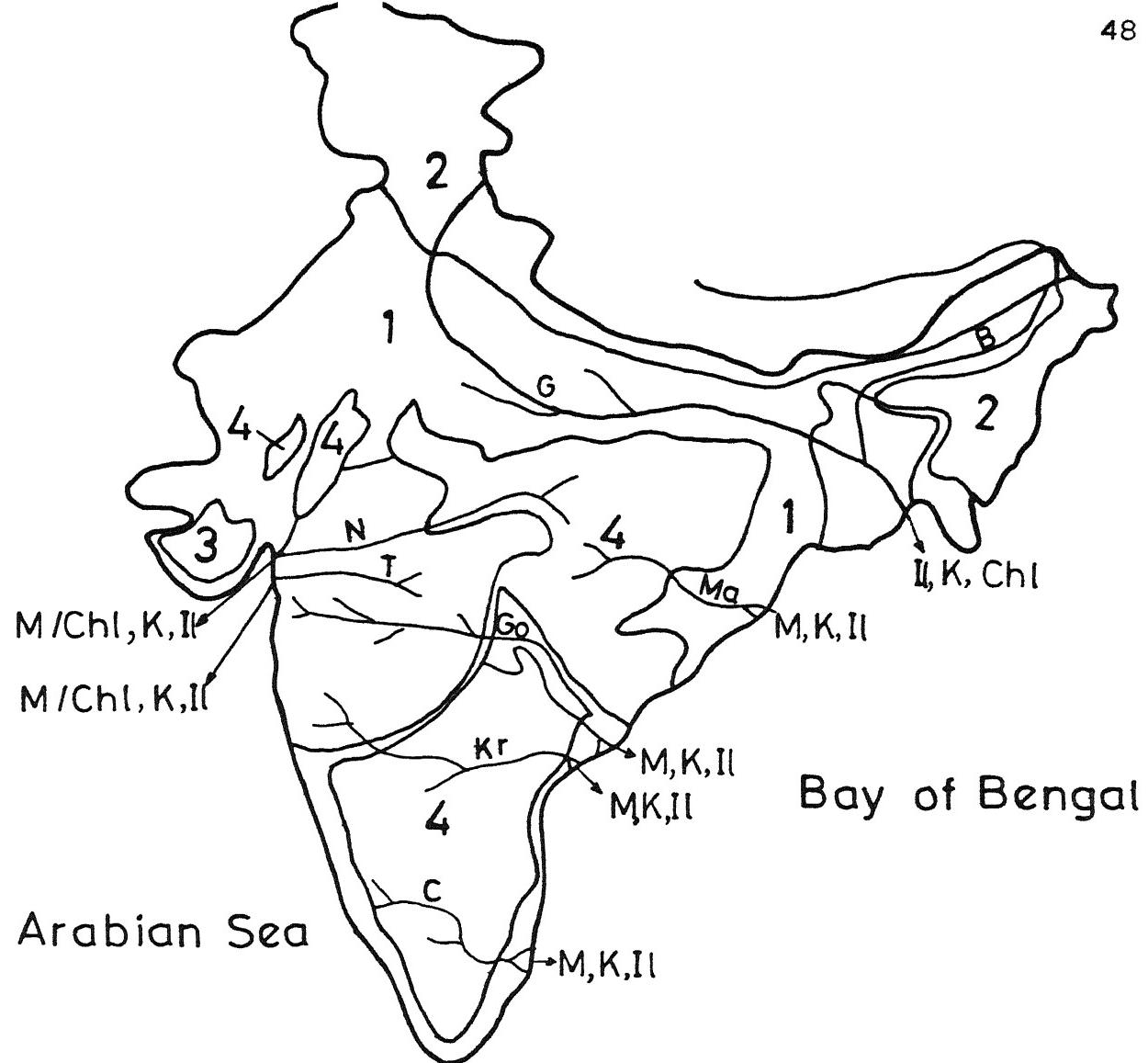
Most of the experimental runs had $P_T = 2 \text{ mg/l} = 2 \times 10^{-5} \text{ m/l}$. A sample calculation at pH 3, 6 and 8 is given in Table 4.6. This would cover the acidified, normal and NaCl-NaHCO_3 buffer solutions. It is seen that the order of dominance is $\text{H}_2\text{PO}_4^- > \text{H}_3\text{PO}_4 > \text{HPO}_4^{-2} > \text{PO}_4^{-3}$ in acidified solution, $\text{H}_2\text{PO}_4^- > \text{HPO}_4^{-2} > \text{H}_3\text{PO}_4 > \text{PO}_4^{-3}$ in normal solution and $\text{HPO}_4^{-2} > \text{H}_2\text{PO}_4^- > \text{PO}_4^{-3} > \text{H}_3\text{PO}_4$ in salt solution. The phosphate species of relevance between river and ocean are H_2PO_4^- and HPO_4^{-2} . In the upper estuary zone, 86 percent of the total dissolved phosphate is in the form of HPO_4^{-2} with -2 charge.

River Input of Clay Minerals into Ocean

The clay minerals which reach the ocean as suspended load in rivers are derived by weathering of bed rock in catchment area. We can illustrate the overall process by taking the specific example of clay minerals in Indian rivers. Fig. 4.1 is a generalised geological map of India on which the major river courses have been superimposed. It is seen that the Himalayan rivers (Ganga and Brahmaputra) drain a terrain dominated by geosynclinal sedimentary rocks and alluvial soils. In contrast, the drainage basins of peninsular rivers like Godavari, Krishna, Narmada and Tapti

Table 4.6 Calculated concentrations (moles/l) of orthophosphate species and average room temperature = 25°C ,
 $P_T = 2 \times 10^{-5}$ moles/l.

	pH = 3	pH = 6	pH = 8
PO_4^{3-}	2.23×10^{-14}	2.36×10^{-8}	3.43×10^{-5}
HPO_4^{2-}	4.46×10^{-9}	4.72×10^{-13}	6.87×10^{-10}
H_2PO_4^-	1.12×10^{-9}	1.18×10^{-6} (5%)	1.72×10^{-5} (86%)
H_3PO_4	1.77×10^{-5} (88%)	1.88×10^{-5} (94%)	2.73×10^{-6} (13%)
	2.23×10^{-6} (11%)	2.36×10^{-9}	3.44×10^{-12}



Rock Types

- Recent deposits
- Himalayan rocks
- Deccan basalt with black cotton soil
- Basement rocks with lateritic soil

Clay Minerals

- | |
|---------------------|
| Chl - Chlorite |
| Il - Illite |
| K - Kaolinite |
| M - Montmorillonite |

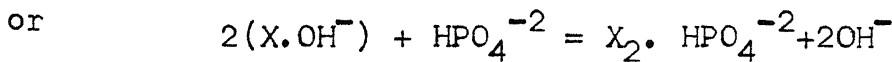
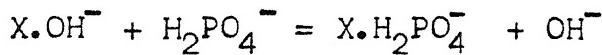
Fig. 4.1 Clay minerals input into ocean from major rivers of India, B= Brahmaputra, C= Cauvery, G= Ganga, Go= Godavari, Kr= Krishna, Ma= Mahanadi, N= Narmada, T= Tapti.

are dominated by Deccan basalts with black cotton soil. Most of the ancient gneissic basement through which Mahanadi and Cauvery flow, has lateritic soil cover. Therefore, the current experiments with kaolinite, laterite and black cotton soil would be applicable to sediment-water interaction at the mouth of major Indian rivers.

The clay mineralogy of Indian river sediments has not been clearly established. There is some controversy over identification of 14 Å clays (Subramanian, 1980; Naidu et al., 1985). Differences have also been reported between suspended and bed sediments as well as fresh water and salt water sediments. However, the broad picture is that the sediments at the mouth of Ganga-Brahmaputra contain illite and kaolinite/chlorite as the main components. On the other hand, the sediments of the peninsular rivers are dominated by montmorillonite/ chlorite with lesser proportion of kaolinite and illite. These data match fairly well with the geology of the drainage basins.

Mechanism of Phosphate Uptake by Clay Minerals

Grim (1967) proposed that exchange of phosphate ion from solution with OH^- ion from clay structure would be one possible mechanism for phosphate fixation by soils. In our experiments, the dominant phosphate ions are H_2PO_4^- or HPO_4^{2-} depending upon pH. Therefore, the exchange reactions with clay would be of the type



where X represents the clay surface.

For such a process, release of OH^- would raise the pH of the solution. This was the case for all the experiments (see Table 4.1 to 4.3) except lateritic soil in salt solution. On the other hand, if the above exchange reaction takes place on equivalent basis, the change in OH^- concentration should match with the change in phosphate. Taking the adsorption by kaolinite - II from normal 2 mg/l solution as an example (Table 4.2),

$$\text{Initial pH} = 6.16 \text{ i.e. } pOH = 7.84$$

$$\text{Final pH} = 7.36 \text{ i.e. } pOH = 6.64$$

$$\Delta OH = 0.21 \times 10^{-3} \text{ me/l}$$

Similarly, initial $PO_4 = 2 \text{ mg/l}$

$$\text{final } PO_4 = 1.7 \text{ mg/l}$$

$$\Delta PO_4 = 0.3 \text{ mg/l} = 0.94 \times 10^{-3} \text{ me/l}$$

Therefore, $\Delta PO_4 > \Delta OH$.

Similar results obtained for other solutions are given in Table 4.7. It is seen that $\Delta PO_4 > \Delta OH$ for adsorption from normal solution by kaolinite, black cotton soil and from salt solution by lateritic soil. On the other hand, $\Delta PO_4 < \Delta OH$ for adsorption from salt solution by kaolinite and black cotton soil. As ΔPO_4 does not equal to ΔOH in these experiments, one-to one exchange between OH and PO_4

Table 4.7 Calculated values of ΔPO_4 and ΔOH

Type of clay Suspension	Initial pH	pOH	Final pH	ΔOH in me/l	PO_4 concentration in mg/l	ΔPO_4 in me/l	Remarks
				Initial	Final		
1. Normal PO_4 solution with kaolinite	6.16	7.84	7.36	6.64	0.21 $\times 10^{-3}$	2	$\Delta PO_4 > \Delta OH$
2. Normal PO_4 solution with black cotton soil	6.16	7.84	7.40	6.6	0.24 $\times 10^{-3}$	2	$\Delta PO_4 > \Delta OH$
3. Normal PO_4 solution with lateritic soil	6.16	7.84	6.27	10.73	0.004 $\times 10^{-3}$	2	$\Delta PO_4 > \Delta OH$
4. Salt solution with kaolinite	8.37	5.63	8.67	5.33	2.3 $\times 10^{-3}$	2	$\Delta PO_4 < \Delta OH$
5. Salt solution with black cotton soil	8.01	5.99	8.36	5.64	1.26 $\times 10^{-3}$	2	$\Delta PO_4 < \Delta OH$
6. Salt solution with lateritic soil	8.13	5.84	7.96	6.04	0.43 $\times 10^{-3}$	2	$\Delta PO_4 > \Delta OH$

is not the only mechanism for phosphate adsorption. In normal solution, physical adsorption may account for additional phosphate uptake. In salt solution, release of OH^- may be balanced jointly by Cl^- and phosphate ($\Delta\text{OH}^- = \Delta\text{Cl} + \Delta\text{PO}_4^-$). On the other hand, positively charged iron oxide colloids in lateritic soil offer sites for phosphate uptake from normal as well as salt solution.

Chemical adsorption (chemisorption) can be compared with physical adsorption in the following way. The fact that in all cases except lateritic soil, a part of the adsorbed phosphate was desorbed indicated that all the phosphate ions did not penetrate deep into the clay structure. Therefore, exchange between OH^- and phosphate ion can not be the only process. The desorbed fraction probably represents the loosely held physically adsorbed phosphate.

The higher adsorption by black cotton soil compared with kaolinite can be attributed to finer grain size (larger specific surface area) of montmorillonite and presence of organic matter.

Adsorption by Lateritic Soil

Due to the presence of positively charged iron oxide/hydroxide colloids the behaviour of lateritic soils is distinct from others. Absence of desorption indicates total chemisorption. Two parallel processes seem to operate (1) exchange of OH^- with H_2PO_4^- and (2) electrostatic attraction of H_2PO_4^- and OH^- ions by positively charged iron oxide colloids. The slight decrease in pH suggests that more

OM^- is picked up by the second process than released by the first. Field data have shown that in estuaries, phosphorous content of sediments is strongly correlated with iron content (Upchurch et al., 1974).

Role of Organic Matter

The lateritic and black cotton soils contained 7.5 and 9.6 percent organic matter. It is highly probable that soil organics play an important role in holding phosphate through complex formation. Sholkovitz (1976) concluded that dissolved organic matter in river and estuary water controls the non-conservative behaviour of inorganic constituents like Fe, Mn, Al and P.

Effect of Salinity

A general feature of these experiments was that phosphate adsorption by kaolinite, lateritic soil and black cotton soil decreased in the presence of salinity (chlorinity) similar to the upper estuary zone. There may be three possible reasons for this result. (1) Less positive sites at higher pH (2) Decrease in specific surface area due to double layer collapse and flocculation accompanied by removal of clay particles by sedimentation (3) Competition between Cl^- and phosphate ions for adsorption on to the clay surface. Such possibilities have been suggested at the Pamlico estuary on

the Atlantic coast of U.S.A. (Upchurch et al., 1974). At this location, the phosphorous content of sediments showed a sharp decline with increasing salinity towards the open sea. It was postulated that phosphorous adsorbed by the clay minerals (kaolinite illite, chlorite and montmorillonite) was released or displaced by competing ions such as Cl and SO₄. Our desorption experiments in salt solution (Table 4.3) supports a similar behaviour by montmorillonite.

CHAPTER 5

CONCLUSIONS

On the basis of this experimental work, the following conclusions can be drawn.

- (1) The materials used in these experiments are typical of weathering products in drainage basins. They form major components of the suspended load in rivers.
- (2) The phosphate level in experimental solutions are of the same order of magnitude as expected in polluted rivers.
- (3) The phosphate solution in $\text{NaCl}-\text{NaHCO}_3$ buffer with ionic strength = 0.3 and pH around 8 can be considered as a simplified version of river water in the upper estuary zone.
- (4) The adsorption capacities of kaolinite clay, black cotton soil and lateritic soil from normal 2 mg/l PO_4 solution were 15%, 42.5% and 100% respectively (Fig. 5.1).
- (5) A part of the phosphate adsorbed by kaolinite and black cotton soil was readily desorbed into distilled water. The percentage of desorption was 33.3 and 16.4 respectively. However, there was no desorption from lateritic soil (Fig. 5.2).
- (6) Desorption from black cotton soil was much more (35.5%) into a salt solution of ionic strength = 0.3 compared with desorption into distilled water (16.4%).

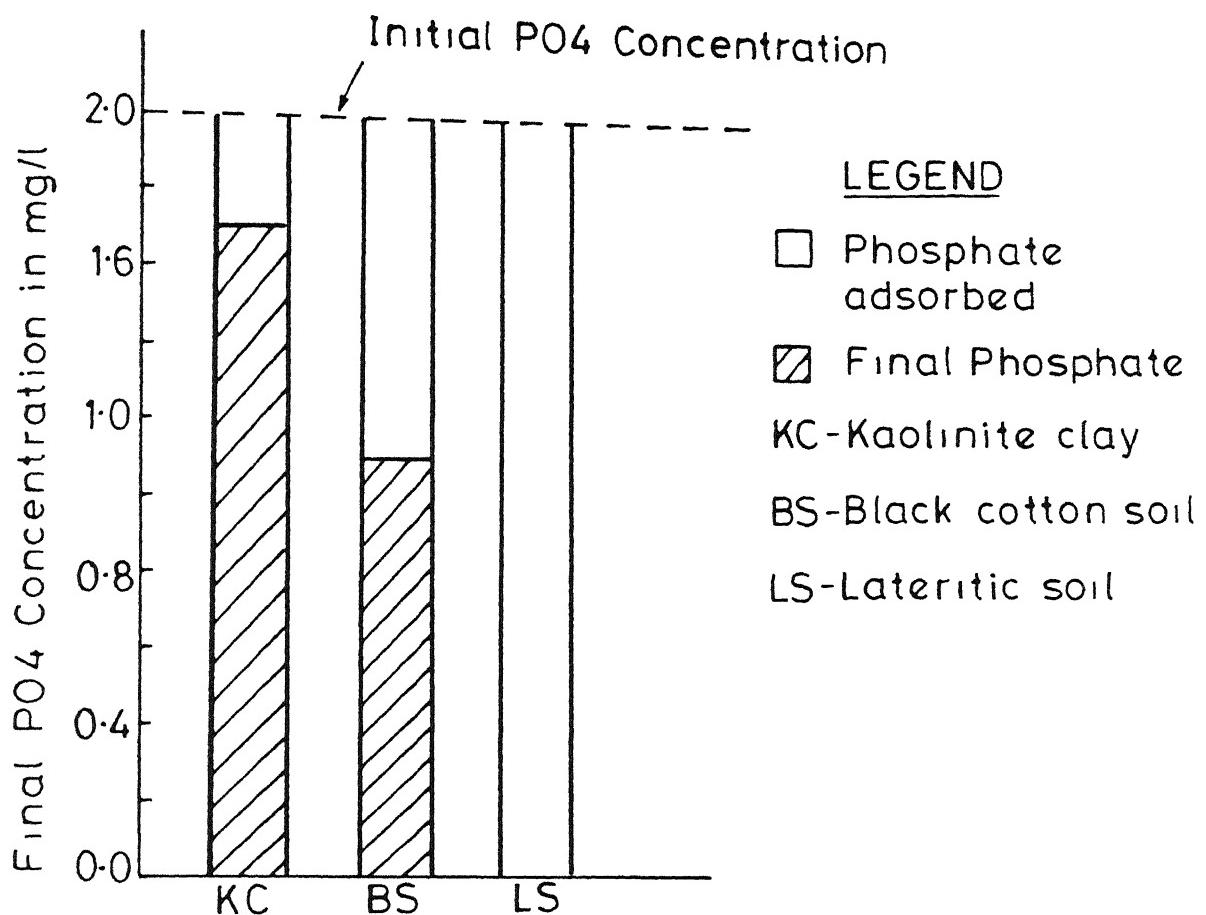


Fig.5.1 Comparison of phosphate uptake by kaolinite clay, black cotton soil and lateritic soil from normal 2 mg/l phosphate solution.

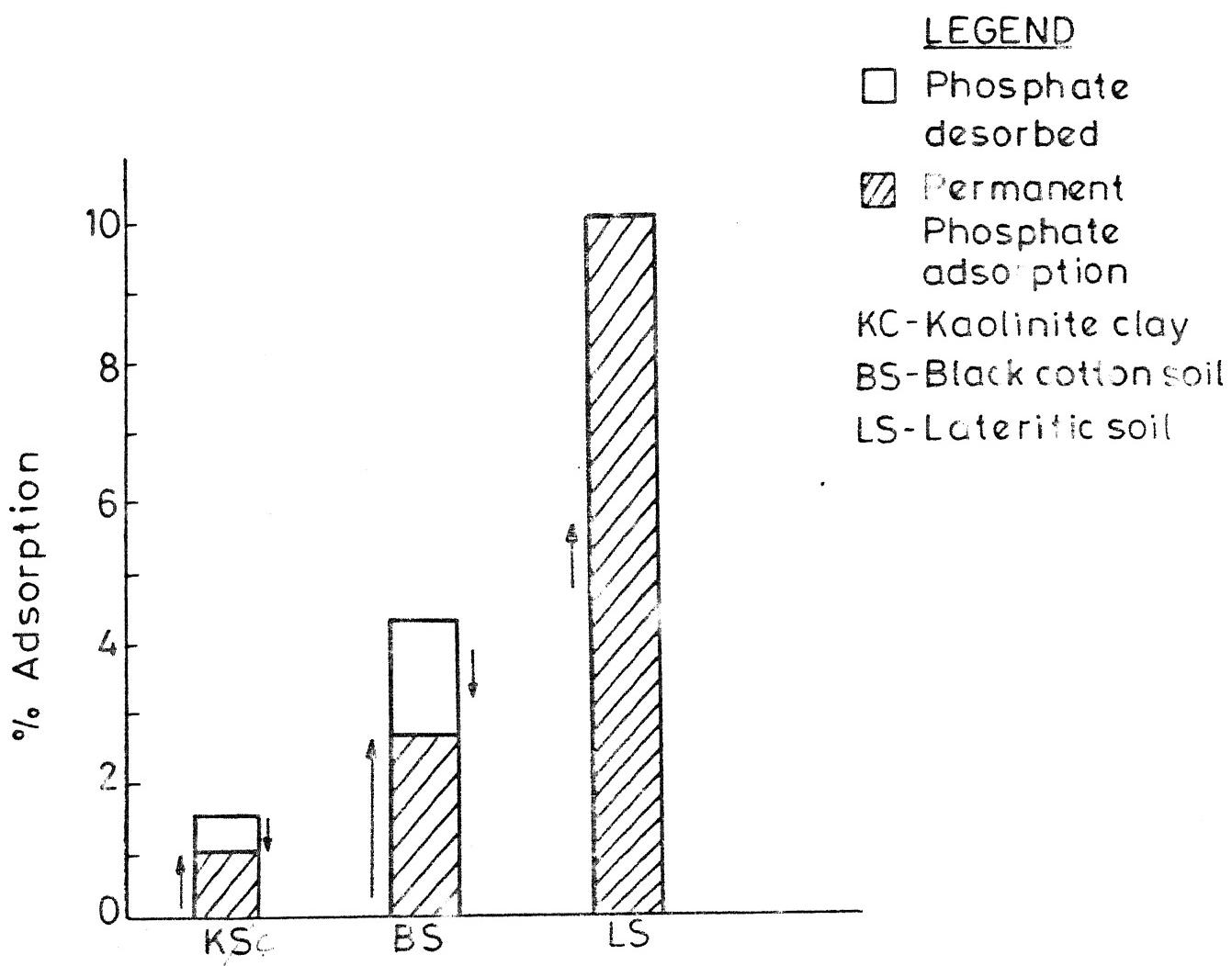


Fig. 5.2 Desorption of adsorbed PO_4^{3-} from kaolinite clay, black cotton soil, and lateritic soil into distilled water

(7) Adsorption from artificial estuary water was less than that from normal phosphate solution. The capacities for kaolinite clay, black cotton soil and lateritic soil were 3.75%, 9.5% and 91% respectively (Fig. 5.3).

(8) The percentage of desorption into distilled after initial adsorption from salt solution was 10.6 for black cotton soil and 9.0 for lateritic soil.

(9) The phosphate-sediment interaction in an actual estuary can be visualised as follows. Phosphate adsorption would be maximum where the suspended load is derived from a lateritic terrain. Most of the phosphate will be permanently held until salinity increases in the upper estuary zone. Adsorption by montmorillonite and kaolinite would be less efficient. The phosphate adsorbed by the sediments in the fresh water zone will be released in saline water. So, eutrophication will be more severe in the mixing zone.

(10) The mechanism of phosphate uptake appears to be a combination of ion exchange (chenisorption) and physical adsorption. The iron oxide colloids in lateritic soil are responsible for its distinct behaviour.

Suggestion for Future Work

Some of the parameters for these preliminary experiments can be refined in the following way.

- (1) Temperature can be more strictly controlled.
- (2) The range of initial phosphate concentration can be widened to collect data for adsorption isotherms.

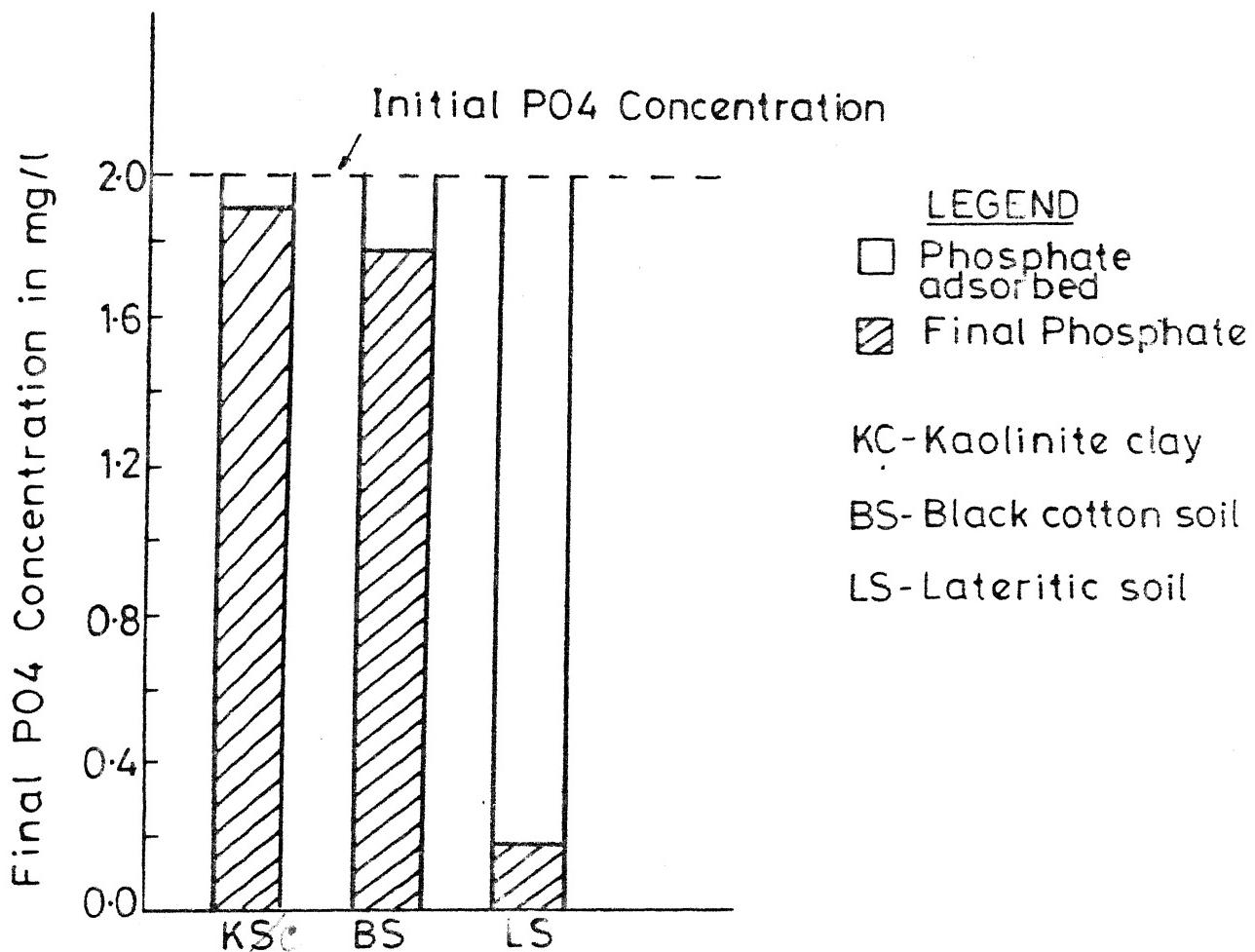


Fig. 5.3 Comparison of adsorption of kaolinite clay, black cotton soil and lateritic soil from PO₄-NaCl-NaHCO₃ solution.

- (3) Other major clay minerals like illite, chlorite can be investigated.
- (4) The grain size and percentage of clay suspension can be varied.
- (5) The uptake of other organic and inorganic anions can be studied. For example, NO_3^- , F^- , detergents and dyes are also important for their environmental impact.

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